

METHOD 10A

DETERMINATION OF SULFUR IN PETROLEUM AND PETROLEUM PRODUCTS

REF: Reg. 9-1-304

2-1-123. 3.2

2-1-123. 3.7

1. PRINCIPLE

- 1.1 The sulfur content of petroleum and petroleum products such as fuel oils, residuals and crude oils is determined by the energy dispersive X-ray fluorescence spectroscopy technique.
- 1.2 The method is fast, non-destructive, and requires minimal sample handling. The sample is placed in the path of a beam radiated from an X-ray tube. The primary X-rays generated by the tube excite sulfur atoms generating fluorescent X-rays; the partial remaining rays are scattered. The fluorescent rays are selectively filtered, and the X-ray detector detects the fluorescent and scattered rays. The detector generates electric pulses that are proportional to the energy of the incoming X-rays. The sulfur concentration is calculated by comparing the counts obtained from the pulses with those of calibration standards.
- 1.3 The limit of detection of this method is 0.05 % sulfur (by weight). The upper limit is 5.00% sulfur (by weight) and can be extended by appropriate dilution.
- 1.4 Samples containing heavy metal additives and lead alkyls may interfere with the test method. Elements such as silicon, phosphorous, calcium, potassium, and halides can interfere at concentrations greater than one tenth of the measured concentration of sulfur, or more than a few hundred milligrams/kilogram. The presence of water, precipitates and solvents with high vapor pressure in the sample matrix may introduce errors in the measurement process. Follow the procedures specified in the manufacturer's "Instruction Manual" when analyzing these types of materials.

2. APPARATUS

- 2.1 Sulfur-in-oil Analyzer: The Horiba Instruments, Inc. SLFA-1100 H model is equipped with an X-ray source.
- 2.2 Sample Holders A and B, disposable sample cells, inner and outer frame of the cell and transparent films. These parts are available from Horiba Instruments, Inc. 17671 Armstrong Avenue, Irvine, CA 92714. Phone: 1-800-4-HORIBA.

3. REAGENTS

- 3.1 National Institute of Standards and Technology (NIST) or other commercially available standards containing 0 to 5 % (by weight) sulfur in various matrices.

4. CALIBRATION

- 4.1 Number of calibration curves: The analyzer can be set to store five calibration curves (1 to 5). Each calibration curve can include up to 20 standards, and has a specific concentration range and matrix. The calibration curve to be used for the analysis is dependent upon sample concentration and matrix, and can be preset in the CONDITION menu. When 'A' for the automatic selection of curve number is entered in the CONDITION menu, the analyzer will automatically use the best fitting curve, based on sample concentration. For setting up of the method, refer to the 'Measurement Conditions' on page 12 of the Horiba Instruction Manual.
- 4.2 Preparation of a calibration curve:
 - 4.2.1 To operate the analyzer and enter data for the standard concentrations, refer to the steps described in the Horiba Instruction Manual page 32 through 39.
 - 4.2.2 Calibration curves can be prepared using one of the following three modes:
 - AUTO: First, key-in the concentration values of the multiple standards, then measure the standards. A calibration curve is obtained automatically from the results of the measurements.
 - MAN 1: Manually enter the coefficients A, B, and C for the calibration curve. This mode is useful when backup battery has run down and the coefficients for the calibration curve are lost from the memory. The coefficients (K) for the curves should be recorded separately.
 - MAN 2: Manually enter both the concentration value and the K value for the calibration curve. This mode can be used when (1) data points need to be added to increase the accuracy of the calibration curve obtained in the AUTO mode, or (2) outlying data points need to be deleted.
 - 4.2.3 Calibrate the analyzer with at least five standards of differing concentrations (0 to 5 % by weight). Refer to pages 14 to 23 of Horiba Instruction Manual for proper calibration of the instrument. Use standards that have the same matrices as the sample.
- 4.3 Degrees of calibration curve: Two degrees of calibration are available, linear and quadratic. Refer to page 15 of Horiba Instruction Manual for appropriate use of degree of calibration.

5. ANALYTICAL PROCEDURE

5.1 Preparation of the Sample Cells:

- 5.1.1 Follow the steps described in the Horiba Instruction Manual page 32 through 34. The amount of sample needed to fill the sample cell is 4-10 mL. **(NOTE 1)**

NOTE 1: Samples that solidify at normal room temperature must be heated until fluid before pouring in the sample cells. Make a pinhole on the paper surface of the sample cell. After ensuring that the sample temperature is back to room temperature, start measurement. Be careful not to heat the samples above 60 °C.

- 5.1.2 Turn on the POWER switch located at the rear of the unit. The READY menu will appear within 60 seconds on the screen. The X-rays lamp will also light up.

5.2 Measurement of the sample concentration:

- 5.2.1 Place the sample cell facing the cell window downward on the cell table.

- 5.2.2 The soft keys F1, F2, F3 and F4 on the panel correspond to COND, ID#, CAL and MAINT on the screen.

- 5.2.3 Press the F1 key to select analytical conditions. Measurement Time is entered in seconds (10, 30, 100, 300 or 600 seconds). Selection of a longer measurement time will generally result in better accuracy of the analysis. However, for the analysis of highly volatile samples select measurement time 10 or 30 seconds to minimize changes in concentration during measurement. Select three repetitions of the measurement. Select a calibration curve (#1, #2, #3, #4, #5 or A). The selection of 'A' will automatically use the appropriate calibration curve based on sample concentration. The automatic selection of the standard curve may not match the sample matrix. **(NOTE 2)**

NOTE 2: It is always best to use standards with matrices and properties closest to those of the samples to be measured. If the calibration is carried out with standards that differ greatly from the sample under measurement, errors may occur.

- 5.2.4 Press the F2 key to enter sample ID#.

- 5.2.5 Press the F4 key to enter date and time in the system.

- 5.2.6 Press 'MEAS' key on the panel to measure the sample. The measurements will be replicated for the previously specified repeat times and each measurement will be continued for the previously entered time. At the end of all replicate measurements, the printer will print sample ID#, Date, Time, # of the calibration curve used, measurement time, repeat times, individual replicate result (wt %s), average of the replicate results (wt %s) and standard deviation.

- 5.2.7 Samples that are out of range: Analytical results over 5.0 % sulfur by weight are out of linear range of the instrument. This may cause errors in analytical results. Therefore, ensure that the concentration of the sample to be measured is within the concentration range of the standards used for calibration. Samples containing more than 5.0 % sulfur by weight can be diluted with a material that is similar to that of the sample matrix.

6. CALCULATIONS

- 6.1 The automatic printout at the end of analysis shows the sample concentration (%S by weight).
- 6.2 If the sample is diluted, multiply the result with the appropriate dilution factor.

7. QUALITY CONTROL

- 7.1 Blank Analysis: A sample of iso-octane is used as a blank and is analyzed before sample analysis to check the analytical system for contamination. If the blank analysis shows a concentration greater than 0.001 wt % sulfur, the blank should be repeated. If the blank still shows sulfur content greater than 0.001 wt %, the contamination source should be corrected before analyzing samples.
- 7.2 Calibration Standard Analysis: Calibration standards are purchased from NIST as needed. The matrix should be similar to that of the sample. The system needs to be recalibrated after a major repair on the instrument (such as X-ray tube replacement), or after a failure to meet requirements on quality control sample and instrument sensitivity.
- 7.3 Control Sample Analysis: The control sample is analyzed at the beginning and at the end of the sample set, and after every 10 samples if the sample set contains more than 10 samples. A control chart is maintained for the control sample. The upper and lower warning limits are set for two standard deviation ($\pm 2\sigma$). The upper and lower control limits are at three standard deviations ($\pm 3\sigma$).
- 7.4 Control sample out-of-control: When the measured value of sulfur in the control sample exceeds the 3σ limit or when two successive measurements of the control sample exceed the 2σ limit, the control sample is called out-of-control. If the Q.C. sample continues to be out-of-control, the calibration and Q.C. sample must be rerun. Determine the cause of the problem before analyzing any samples, if the control sample continues to be out-of-control.
- 7.5 Replicate Analysis: The instrument automatically performs three replicate analyses during the measurement. The printout includes individual and average reading of the replicates. The Horiba SLFA-1100 H model is also capable of performing 5 or 10 replicates during measurement. If the

closest two values of the three analyses show a difference that is greater than five %, all the samples analyzed after the previous replicate must be reanalyzed. Corrective action should be taken to determine the cause of the problem.

8. REFERENCES

- 8.1 Horiba Instruction Manual – Horiba LTD.
- 8.2 “Standard Test Method for Sulfur in Petroleum and Petroleum Products by Energy Dispersive X-Ray Fluorescence Spectrometry” ASTM Designation D 4294-98, Book of ASTM Standards, Volume 5.02, 1998.